



Australian Government

Department of the Environment and Heritage



National Pollutant Inventory

**Emission Estimation
Technique Manual
for
Lime and Dolomite
Manufacturing
Version 1.1
16 September 2003**

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Erratum for Lime and Dolomite Manufacturing EET Manual (Version 1.1 - 16 September 2002).

Page	Outline of alteration
All tables	Clarified data by providing in scientific notation and correcting the names of some pollutants.
22 - Table 8	Corrected factor for some organics (e.g. polychlorinated dioxins and furans).

**EMISSION ESTIMATION TECHNIQUES
FOR
LIME AND DOLOMITE MANUFACTURING**

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LIME AND DOLOMITE MANUFACTURING

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1. Introduction

The purpose of all Emission Estimation Technique (EET) Manuals in this series is to assist Australian manufacturing, industrial and service facilities to report emissions of listed substances to the National Pollutant Inventory (NPI). This Manual describes the procedures and the recommended approaches for estimating emissions from facilities engaged in lime and dolomite manufacturing.

The lime manufacturing activities covered in this Manual apply to facilities primarily engaged in the manufacture of quick, hydrated, and agricultural lime and limestone products, and dolomite.

EET MANUAL: Lime and Dolomite Manufacturing

HANDBOOK: Cement & Lime Manufacturing

ANZSIC CODES : 2631 and all codes within the 263 ANZSIC code group.

This Manual was drafted by the NPI Unit of the Queensland Department of Environment and Heritage on behalf of the Commonwealth Government. It has been developed through a process of national consultation involving State and Territory environmental authorities and key industry stakeholders.

2. Process Description

The following section presents a brief description of the lime and dolomite Industry and identifies likely sources of emissions.

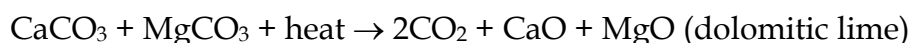
2.1 General Processes

This Section describes the major industrial processes within the lime products manufacturing industry, including the materials, equipment used and the processes employed. The Section is designed to provide a general understanding of the industry and the inter-relationship between the industrial process and the topics discussed in subsequent Sections of the Manual - emissions of NPI-listed substances, estimating emissions, control technologies and emission abatement.

This Section specifically contains a description of commonly used production processes, associated raw materials, the by-products produced, NPI-listed substances emitted, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provides a concise description of where emissions may be produced in the process. This Section also describes the potential fate - to air, water, or land - of these emissions and waste products.

Lime is a product derived from high temperature calcination of limestone. Although limestone deposits are very common throughout Australia and deposits exist in all states, only a small portion of these deposits is pure enough for industrial and agricultural lime manufacturing. To be classified as limestone, the rock must contain at least 50 percent calcium carbonate. When the rock contains 30 to 45 percent magnesium carbonate, it is referred to as dolomite or dolomitic limestone. Lime can also be produced from aragonite, chalk, coral, marble, and sea shells.

Lime is manufactured in various kinds of kilns by one of the following reactions:



Major uses of lime are metallurgical (steel, copper, gold, aluminium, and silver), environmental (flue gas desulfurisation, water softening and pH control, sewage-sludge stabilisation, hazardous waste treatment, acid neutralisation), for construction purposes (soil stabilisation, bitumen additive, and masonry lime), and agricultural (soil conditioning and pH control).

In some lime plants, the resulting lime is reacted (slaked) with water to form hydrated lime. The basic processes in the production of lime are:

- (1) quarrying raw limestone;
- (2) preparing limestone for the kilns by crushing and sizing;
- (3) calcining limestone;
- (4) processing the lime further by hydrating; and
- (5) miscellaneous transfer, storage, and handling operations.

In some lime plants, a by-product of lime manufacturing is ground limestone for agricultural purposes (aglime). The grinding of this product can be a source of PM₁₀ emissions (particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less ie. $\leq 10\mu\text{m}$).

A generalised material flow diagram for a lime manufacturing plant is given in Figure 1, although some operations depicted may not be performed at all facilities. As each facility in Australia is likely to be different from any other facility, you are strongly encouraged to develop a flow diagram for your particular operations that details the input of materials and listed substances and the waste sources and emissions resulting from each process.

2.1.1 Rotary and Vertical Kilns

The heart of a lime plant is the kiln with the prevalent type being the rotary kiln, which accounts for about 90 percent of all lime production in Australia. The kiln is a long, cylindrical, slightly inclined, refractory-lined furnace, through which the limestone and combustion gases pass counter-currently. Coal, oil, and natural gas may all be fired in rotary kilns. Product coolers and kiln feed preheaters are commonly used to recover heat from the hot lime product and exhaust gases.

The next most common type of kiln in Australia is the vertical, or shaft, kiln. This kiln can be described as an upright heavy steel cylinder lined with refractory material. The limestone is charged at the top and is calcined as it descends slowly to discharge at the bottom of the kiln. A primary advantage of vertical kilns over rotary kilns is their higher average fuel efficiency. The primary disadvantages of vertical kilns are their relatively low production rates and the fact that coal cannot be used without degrading the quality of the lime produced.

Other, much less common, kiln types include rotary hearth and fluidised bed kilns. Both kiln types can achieve high production rates, with fluidised bed kilns sometimes operating on coal. The calcimatic kiln, or rotary hearth kiln, is a circular kiln with a slowly revolving doughnut-shaped hearth. In fluidised bed kilns, finely divided limestone is brought into contact with hot combustion air in a turbulent zone, usually above the perforated grate. Because of the amount of lime carryover into the exhaust gas, dust collection equipment must be installed on fluidised bed kilns for process economy.

2.1.2 Parallel Flow Regenerative Kilns

Another alternative process that has recently emerged in Australia is the parallel flow regenerative (PR) lime kiln. This process combines two advantages. First, optimum heating conditions for lime calcining are achieved by concurrent flow of the charge material and combustion gases. Second, the multiple-chamber regenerative process uses the charge material as the heat transfer medium to preheat the combustion air. The basic PR system has two shafts, but the shaft systems are used with small size grains to address the increased flow resistance associated with smaller feed sizes.

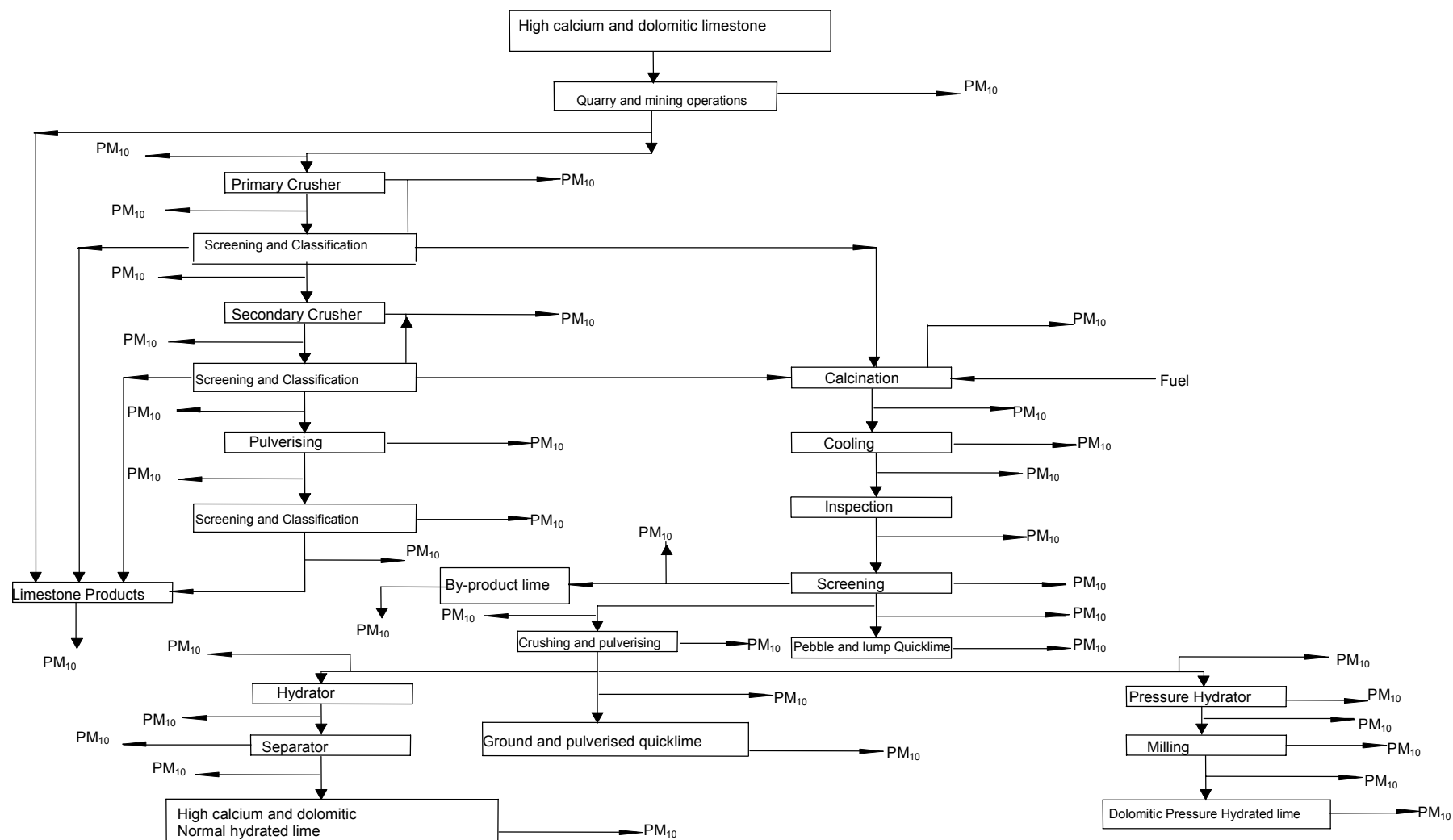


Figure 1 - Process Flow Diagram of a Lime Manufacturer
 (Adapted from USEPA AP-42 Section 11.17 1996)

In the two-shaft system, the shafts alternate functions, with one shaft serving as the heating shaft and the other as the flue gas shaft. Limestone is charged alternatively into the two shafts and flows downward by the influence of gravity. Each shaft includes a heating zone, a combustion zone, and a cooling zone. The two shafts are connected in the middle to allow gas flow between them. In the heated shaft, combustion air flows downward through the heated charge material. After being preheated by the charge material, the combustion air combines with the fuel and then the fuel mixture is fired downward into the combustion zone. The hot combustion gases pass from the combustion zone into the heating shaft to the combustion zone in the flue gas shaft. The heated exhaust gases flow upward through the flue gas shaft combustion zone and into the preheating zone where they heat the charge material. The function of the two shafts reverses on a 12-minute cycle. The bottom of both shafts is a cooling zone. Cooling air flows upward through the shaft counter-currently to the flow of the calcined product. This air mixes with the combustion gases in the crossover area providing additional combustion air. The product flows by the force of gravity from the bottom of both shafts.

About 15 percent of all lime produced in Australia is converted to hydrated, or slaked, lime. There are two kinds of hydrators: atmospheric and pressure. Atmospheric hydrators, the more prevalent type, are used in continuous mode to produce high-calcium and dolomitic hydrates. Pressure hydrators, on the other hand, only produce exclusively a completely hydrated dolomitic lime and operate in batch mode. Generally, water sprays or wet scrubbers perform the hydrating process and prevent product loss. Following hydration, the product may be milled and then conveyed to air separators for further drying and removal of coarse fractions.

3. Emission Sources and Control Technologies

3.1 Emissions to Air

Air emissions may be categorised as:

Fugitive Emissions

These are emissions that are not released through a vent or stack. Examples of fugitive emissions include dust from stockpiles, volatilisation of vapour from vats, open vessels, or spills and materials handling. Emissions emanating from ridgeline roof-vents, louvres, and open doors of a building as well as equipment leaks, and leaks from valves and flanges are also examples of fugitive emissions. Emission factor EETs are the usual method for determining losses through fugitive emissions.

Point Source Emissions

These emissions are exhausted into a vent (excluding roof vents) or stack and emitted through a single point source into the atmosphere. Table 1 highlights common air emissions from lime and dolomite manufacturing processes.

Table 1 - Common NPI Air Emissions from Lime and Dolomite Manufacturing¹

NPI Substances	
Acetone	Hydrochloric acid
Ammonia (& ammonium salts)	Lead & compounds
Arsenic & compounds	Manganese & compounds
Benzene	Mercury & compounds
Beryllium & compounds	Methyl ethyl ketone
Cadmium & compounds	Oxides of nitrogen (NO _x)
Carbon disulfide	Particulate matter 10 microns or less in diameter (PM ₁₀)
Carbon monoxide (CO)	Phenol
Chlorine	Polychlorinated dioxins and furans
Chlorobenzene	Polycyclic aromatic hydrocarbons (PAHs)
Chromium (III) compounds	Selenium & compounds
Copper & compounds	Styrene
Di-(2-ethylhexyl) phthalate (DEHP)	Sulfur dioxide (SO ₂)
Dichloromethane	Sulfuric acid
Ethylbenzene	Toluene
Fluoride compounds	Xylenes
Formaldehyde	Zinc & compounds
<u>Notes:</u>	
1. Source: Queensland Department of Environment and Heritage, 1998.	

Air emission control technologies, such as electrostatic precipitators, fabric filters or baghouses, and wet scrubbers, are commonly installed to reduce the concentration of particulates in process off-gases before stack emission. Where such emission abatement equipment has been installed, and where emission factors from uncontrolled sources have been used in emission estimation, the collection efficiency of the abatement equipment needs to be considered. Guidance on applying collection efficiencies to emission factor equations is provided in later sections.

With regards to emission controls for PM₁₀, in the absence of measured data, or knowledge of the collection efficiency for a particular piece of equipment, an efficiency of 90% should be used in the emission factor equation to calculate actual mass emissions. This default should only be used if there is no other available control efficiency.

3.2 Emissions to Water

Emissions of substances to water can be categorised as discharges to:

- Surface waters (eg. lakes, rivers, dams, and estuaries); and
- Coastal or marine waters.

Because of the significant environmental hazards posed by emitting toxic substances to water, most facilities emitting NPI-listed substances to waterways are required by their relevant State or Territory environment agency to closely monitor and measure these emissions. This existing sampling data can be used to calculate annual emissions.

If no wastewater monitoring data exists, emissions from process water can be calculated based on a mass balance or using emission factors.

The discharge of listed substances to a sewer or tailings dam does not require you to report to the NPI. However, leakage and other emissions (including dust) from a tailings storage facility are reportable. (See also Section Three of *The NPI Guide*.)

3.3 Emissions to Land

Emissions of substances to land on-site include solid wastes, slurries, sediments, spills and leaks, storage and distribution of liquids and may contain listed substances. These emission sources can be broadly categorised as:

- surface impoundments of liquids and slurries; and
- unintentional leaks and spills.

The discharge of wastes to land is monitored by the relevant State or Territory environmental agency.

4. Emission Estimation Techniques

Estimates of emissions of NPI-listed substances to air, water and land should be reported for each substance that triggers a threshold. The reporting list and detailed information on thresholds are contained in *The NPI Guide* at the front of this Handbook.

In general, there are four types of emission estimation techniques (EETs) that may be used to estimate emissions from your facility. The four types described in the *NPI Guide* are:

- sampling or direct measurement;
- mass balance;
- fuel analysis or other engineering calculations; and
- emission factors.

Select the EET (or mix of EETs) that is most appropriate for your purposes. For example, you might choose to use a mass balance to best estimate fugitive losses from pumps and vents, direct measurement for stack and pipe emissions, and emission factors when estimating losses from storage tanks and stockpiles.

If you estimate your emission by using any of these EETs, your data will be displayed on the NPI database as being of 'acceptable reliability'. Similarly, if your relevant environmental authority has approved the use of emission estimation techniques that are not outlined in this Handbook, your data will also be displayed as being of 'acceptable reliability'.

This Manual seeks to provide the most effective emission estimation techniques for the NPI substances relevant to this industry. However, the absence of an EET for a substance in this Manual does not necessarily imply that an emission should not be reported to the NPI. The obligation to report on all relevant emissions remains if reporting thresholds have been exceeded.

You are able to use emission estimation techniques that are not outlined in this document. You must, however, seek the consent of your relevant environmental authority. For example, if your company has developed site-specific emission factors, you may use these if approved by your relevant environmental authority.

In general, direct measurement is the most accurate method for characterising emissions and, where available, such data should be used in preference to other EETs presented in this Manual. However, additional direct measurement is not required under the NPI Measure. Direct monitoring may be undertaken as an element of other EETs.

You should note that the EETs presented in this Manual relate principally to average process emissions. Emissions resulting from non-routine events are rarely discussed in the literature, and there is a general lack of EETs for such events. However, it is important to recognise that emissions resulting from significant operating excursions and/or accidental situations (eg. spills) will also need to be estimated. Emissions to land, air and water from spills must be estimated and added to process emissions when calculating total emissions for reporting purposes. The emission resulting from a spill is the net emission, ie. the quantity of the NPI reportable substance spilled, less the quantity recovered or consumed

during clean up operations.

The **usage*** of each of the substances listed as Category 1 and 1a under the NPI must be estimated to determine whether the 10 tonnes (or 25 tonnes for Total Volatile Organic Compounds, VOCs) reporting threshold is exceeded. If the threshold is exceeded, **emissions** of these Category 1 and 1a substances must be reported for all operations/processes relating to the facility, even if the actual emissions of the substances are very low or zero.

* Usage is defined as meaning the handling, manufacture, import, processing, coincidental production or other uses of the substances.

Table 2 lists the variables and symbols used throughout this Manual.

Table 2 - List of Variables and Symbols

Variable	Symbol	Units
Concentration	C	parts per million volume dry, ppmvd
Molecular weight	MW	kg/kg-mole
Molar volume @ STP (standard temperature and pressure)	V	22.4 m ³ /kg-mole @ 0°C and 101.3 kPa
Volumetric flow rate of stack gas	Q _w	wet cubic metres per second (m ³ /s)
Volumetric flow rate of stack gas	Q _d	dry cubic metres per second (m ³ /s)
Total emissions of pollutant I per hour	E _I	kg/hr
Annual emissions of pollutant I	E _{kpy,I}	kg/yr
Filter catch	C _f	grams (g)
Fuel use	Q _f	kg/hr
PM ₁₀ concentration	C _{PM}	grams/m ³
Metered volume at standard temperature and pressure	V _{m, STP}	m ³
Moisture collected	g _{moist}	grams
Moisture in exhaust gas (wet)	moist _r	%
Temperature	T	°Celsius, <i>specify °C (or absolute temperature, K) in each equation</i>
Clinker production (Activity rate)	A	tonnes/hour
Annual operating hours	OpHrs	hours/year
Wind speed	U	m/sec
Emission factor for pollutant I	EF _I	kg/t, kg/area, and/or kg/vehicle km travelled,
Overall control efficiency ^a (ie Emission reduction control factor)	CE _I	% reduction in emissions of pollutant I
No of wheels for vehicle	NW	
Vehicle kilometre travelled	VKT	vehicle

Source: Queensland Department of Environment and Heritage, 1998.

^a Some users may be accustomed to using Emission Reduction (ER)

4.1 Sampling Data or Direct Measurement

You may wish to undertake direct measurement in order to report to the NPI, particularly if you already do so in order to meet other regulatory requirements. However, the NPI does not require you to undertake additional sampling and measurement.

Stack sampling test reports often provide emissions data in terms of kg/hr or g/m³ (dry). Annual emissions for NPI reporting can be calculated from this data using Equation 1 or Equation 2 following. Stack tests for NPI reporting should be performed under representative (ie. normal) operating conditions. You should be aware that some tests undertaken for a State or Territory license condition may require the test be taken under maximum emissions rating, where emissions are likely to be higher than when operating under normal operating conditions.

This section shows how to calculate emissions in kg/hr based on stack sampling data and how to convert this to an annual emissions figure. Calculations involved in determining PM₁₀ emissions are used as an example, although the same calculations are applicable for most of the substances listed on the Inventory.

An example of test results is summarised in Table 3. The table shows the results of three different sampling runs conducted during one test event. The source parameters measured as part of the test run include gas velocity and moisture content, which are used to determine exhaust gas flow rates in m³/s. The filter weight gain is determined gravimetrically and divided by the volume of gas sampled, as shown in Equation 1 to determine the PM concentration in grams per m³. Note that this example does not present the condensable PM emissions.

Pollutant concentration is then multiplied by the volumetric flow rate to determine the emission rate in kilograms per hour, as shown in Equation 2 and Example 1.

Equation 1

$$C_{PM} = C_f / V_{m,STP}$$

where:

C_{PM}	=	concentration of PM or gram loading, g/m ³
C_f	=	filter catch, g
$V_{m,STP}$	=	metered volume of sample at STP, m ³

Equation 2

$$E_{PM} = C_{PM} * Q_d * 3.6 * [273 / (273 + T)]$$

where:

E_{PM}	=	hourly emissions of PM, kg/hr
C_{PM}	=	concentration of PM or gram loading, g/m ³
Q_d	=	stack gas volumetric flow rate, m ³ /s, dry
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
T	=	temperature of the gas sample, °C

Table 3 - Stack Sample Test Results

Parameter	Symbol	Test 1	Test 2	Test 3
Total sampling time (sec)		7.2E+03	7.2E+03	7.2E+03
Moisture collected (g)	g_{MOIST}	3.956E+02	3.726E+02	3.414E+02
Filter catch (g)	C_f	8.51E-02	4.49 E-02	6.25 E-02
Average sampling rate (m ³ /s)		1.67E-04	1.67E-04	1.67E-04
Standard metered volume (m ³)	$V_{m, STP}$	1.185	1.160	1.163
Volumetric flow rate (m ³ /s), dry	Q_d	8.48	8.43	8.45
Concentration of particulate (g/m ³)	C_{PM}	7.18E-02	3.87E-02	5.37E-02
<u>Notes:</u> 1. Source: Queensland Department of Environment and Heritage 1998. 2. Scientific notation is used; e.g. 7.38E-02 represents 7.38 x 10 ⁻² or 0.0738 and 7.38E+02 represents 7.38 x 10 ⁺² or 738.				

Example 1 - Using Stack Sampling Data

PM emissions calculated using Equation 1 and Equation 2 and the stack sampling data for Test 1 (presented in Table 3, and an exhaust gas temperature of 150°C (423 K)). This is shown below:

$$\begin{aligned} C_{PM} &= C_f / V_{m, STP} \\ &= 0.0851 / 1.185 \\ &= 0.072 \text{ g/m}^3 \\ \\ E_{PM} &= C_{PM} * Q_d * 3.6 * [273 / (273 + T)] \\ &= 0.072 * 8.48 * 3.6 * (273 / 423 \text{ K}) \\ &= 1.42 \text{ kg/hr} \end{aligned}$$

The information from some stack tests may be reported in grams of particulate per cubic metre of exhaust gas (wet). Use Equation 3 to calculate the dry particulate emissions in kg/hr.

Equation 3

$$E_{PM} = Q_w * C_{PM} * 3.6 * \left(1 - \frac{moist_R}{100}\right) * \left[\frac{273}{273 + T}\right]$$

where:

E_{PM}	=	hourly emissions of PM in kilograms per hour, kg/hr
Q_w	=	wet cubic metres of exhaust gas per second, m ³ /s
C_{PM}	=	concentration of PM or gram loading, g/m ³
3.6	=	3600 seconds per hour multiplied by 0.001 kilograms per gram
$moist_R$	=	moisture content, %
273	=	273 K (0°C)
T	=	stack gas temperature, °C

Total suspended particulates (TSP) are also referred to as total particulate matter (total PM). To determine PM₁₀ from total PM emissions, it may be necessary for facility operators to first undertake a size analysis of the stack filter catch. The weight PM₁₀ fraction can then be multiplied by the total PM emission rate to produce PM₁₀ emissions. Alternatively, assume that 100% of PM emissions are PM₁₀; ie assume that all particulate matter emitted to air has an equivalent aerodynamic diameter of 10 micrometres or less ie. ≤10µm.

To calculate moisture content use Equation 4

Equation 4

Moisture percentage = 100 % * weight of water vapour per specific volume of stack gas/ total weight of the stack gas in that volume.

$$moist_R = \frac{100 \% * \left(\frac{g_{moist}}{(1000 * V_{m,STP})}\right)}{\left(\frac{g_{moist}}{(1000 * V_{m,STP})}\right) + \rho_{STP}}$$

where:

$moist_R$	=	moisture content, %
g_{moist}	=	moisture collected, g
$V_{m,STP}$	=	metered volume of sample at STP, m ³
ρ_{STP}	=	dry density of stack gas sample, kg/m ³ at STP {if the density is not known a default value of 1.62 kg/m ³ may be used. This assumes a dry gas composition of 50% air, 50% CO ₂ }

Example 2 - Calculating Moisture Percentage

A 1.2m³ sample (at STP) of gas contains 410g of water. To calculate the moisture percentage use Equation 4.

$$moist_R = \frac{100 \% * \left(\frac{g_{moist}}{1000 * V_{m,STP}} \right)}{\left(\frac{g_{moist}}{1000 * V_{m,STP}} \right) + \rho_{STP}}$$

$$\begin{aligned} g_{MOIST} / 1000 * V_{m,STP} &= 410 / (1000 * 1.2) \\ &= 0.342 \\ moist_R &= 100 * 0.342 / (0.342 + 1.62) \\ &= 17.4\% \end{aligned}$$

In some lime plants, a by-product of lime manufacture is ground limestone for agricultural purposes (Aglime). The grinding of this product is a potential source of PM₁₀ emissions.

4.1.1 Continuous Emission Monitoring System (CEMS) Data

A continuous emission monitoring system (CEMS) provides a continuous record of emissions over time, usually by reporting pollutant concentration. Once the pollutant concentration is known, emission rates are obtained by multiplying the pollutant concentration by the volumetric gas or liquid flow rate of that pollutant.

To monitor SO₂, NO_x, VOC, and CO emissions using a CEMS, you use a pollutant concentration monitor that measures the concentration in parts per million by volume dry air (ppm_{vd} = volume of pollutant gas/10⁶ volumes of dry air). Flow rates should be measured using a volumetric flow rate monitor. Flow rates estimated based on heat input using fuel factors may be inaccurate because these systems typically run with high excess air to remove the moisture out of the kiln. Emission rates (kg/hr) are then calculated by multiplying the stack gas concentrations by the stack gas flow rates.

Table 4 presents example CEM data output for three periods for a hypothetical kiln. The output includes pollutant concentrations in parts per million dry basis (ppm_{vd}), diluent (O₂ or CO₂) concentrations in percent by volume dry basis (%v, d) and gas flow rates; and may include emission rates in kilograms per hour (kg/hr). This data represents a snapshot of a hypothetical kiln operation. While it is possible to determine total emissions of an individual pollutant over a given time period from this data, assuming the CEM operates properly all year long, an accurate emission estimate can be made by adding the hourly emission estimates if the CEMS data is representative of typical operating conditions.

Although CEMS can report real-time hourly emissions automatically, it may be necessary to estimate annual emissions from hourly concentration data manually. This Section describes how to calculate emissions for the NPI from CEMS concentration data. The selected CEMS data should be representative of operating conditions. When possible, data collected over longer periods should be used.

It is important to note that prior to using CEMS to estimate emissions, you should develop a protocol for collecting and averaging the data in order that the estimate satisfies the local environmental authority's requirement for NPI emissions estimations.

Table 4 - Example CEMS Output for an Hypothetical Kiln Firing Waste Fuel Oil¹

Time	O ₂ (% by volume)	Concentration (C) (ppm _{vd})				Gas Flow	Lime Production Rate (A)
		SO ₂	NO _x	CO	VOC	Rate Q(m ³ /s)	(tonnes/ hour)
1	10.3	150.9	142.9	42.9	554.2	8.52	290
2	10.1	144.0	145.7	41.8	582.9	8.48	293
3	11.8	123.0	112.7	128.4	515.1	8.85	270
Notes:							
1. Source: Queensland Department of Environment and Heritage, 1998.							

Hourly emissions can be based on concentration measurements as shown in Equation 5.

Equation 5

$$E_i = (C * MW * Q_d * 3600) / [22.4 * (T + 273/273) * 10^6]$$

where:

E _i	=	emissions of pollutant i, kg/hr
C	=	pollutant concentration, ppm _{v,d}
MW	=	molecular weight of the pollutant, kg/kg-mole
Q _d	=	stack gas volumetric flow rate, m ³ /s
3600	=	conversion factor, s/hr
22.4	=	volume occupied by one mole of gas at standard temperature and pressure (0°C and 101.3 kPa), m ³ /kg-mole
T	=	temperature of gas sample, °C

Actual annual emissions can be calculated by multiplying the emission rate in kg/hr by the number of actual operating hours per year (OpHrs) as shown in Equation 6 for each typical time period and summing the results.

Equation 6

$$E_{kpy,i} = \sum (E_i * OpHrs)$$

where:

E _{kpy,i}	=	annual emissions of pollutant i, kg/yr
E _i	=	emissions of pollutant i, kg/hr (from Equation 5)
OpHrs	=	operating hours, hr/yr

Emissions in kilograms of pollutant per tonne of lime produced can be calculated by dividing the emission rate in kg/hr by the activity rate (lime production rate, tonnes/hr) during the same period (Equation 7) as shown below. It should be noted that the emission factor calculated below assumes that the selected time period (ie. hourly) is representative of annual operating conditions and longer time periods should be used for NPI reporting where they are available.

Equation 7

$$E_{kpt,i} = E_i / A$$

where:

$$\begin{aligned} E_{kpt,i} &= \text{emissions of pollutant i per tonne of lime} \\ &\quad \text{produced, kg/t} \\ E_i &= \text{hourly emissions of pollutant i, kg/hr} \\ A &= \text{lime production, t/hr} \end{aligned}$$

Example 3 illustrates the application of Equation 5, Equation 6, and Equation 7.

Example 3 - Using CEMS Data

This example shows how SO₂ emissions can be calculated using Equation 5 based on the CEMS data for Time Period 1 shown in Table 4, and an exhaust gas temperature of 150°C (423 K).

$$\begin{aligned} E_{SO_2,1} &= (C * MW * Q * 3\,600) / [(22.4 * (T+273/273) * 10^6] \\ &= (150.9 * 64 * 8.52 * 3\,600) / [22.4 * (423/273) * 10^6] \\ &= 296\,217\,907 / 34\,707\,692 \\ &= 8.53\text{kg/hr} \end{aligned}$$

For Time Period 2, also at 150°C

$$E_{SO_2,2} = 8.11\text{kg/hr}$$

For Time Period 3, also at 150°C

$$E_{SO_2,3} = 7.23\text{kg/hr}$$

Say representative operating conditions for the year are:

$$\begin{aligned} \text{Period 1} &= 1500 \text{ hr} \\ \text{Period 2} &= 2000 \text{ hr} \\ \text{Period 3} &= 1800 \text{ hr} \end{aligned}$$

Total emissions for the year are calculated by adding the results of the three Time Periods using Equation 6:

$$\begin{aligned} E_{kpy,SO_2} &= E_{SO_2,1} * \text{OpHrs} + E_{SO_2,2} * \text{OpHrs} + E_{SO_2,3} * \text{OpHrs} \\ &= (8.53 * 1500) + (8.11 * 2000) + (7.23 * 1800) \text{ kg} \\ &= 42\,021 \text{ kg/yr} \end{aligned}$$

Emissions, in terms of kg/tonne of lime produced when operating in the same mode as time period 1, can be calculated using Equation 7:

$$\begin{aligned} E_{kpt,SO_2} &= E_{SO_2} / A \\ &= 8.53 / 290 \\ &= 2.94 * 10^{-2} \text{ kg SO}_2 \text{ emitted per tonne of lime produced} \end{aligned}$$

When the kiln is operating as in time periods 2 or 3, similar calculations can be undertaken for emissions per tonne.

4.2 Mass Balance

A mass balance identifies the quantity of substance going in and out of an entire facility, process, or piece of equipment. Emissions can be calculated as the difference between input and output of each listed substance. Accumulation or depletion of the substance within the equipment should be accounted for in your calculation.

4.3 Engineering Calculations

An engineering calculation is an estimation method based on physical/chemical properties (eg. vapour pressure) of the substance and mathematical relationships (eg. ideal gas law).

4.3.1 Fuel Analysis

Fuel analysis is a particular type of engineering calculation and can be used to predict SO₂, metals, and other emissions based on application of conservation laws, if fuel rate is measured. The presence of certain elements in fuels may be used to predict their presence in emission streams. This includes elements such as sulfur, which may be converted into other compounds during the combustion process.

The basic equation used in fuel analysis emission calculations is the following:

Equation 8

$$E_{kpy,i} = Q_f * \text{pollutant concentration in fuel}/100 * (MW_p / EW_f) * OpHrs$$

where:

$E_{kpy,i}$	=	emissions of pollutant i, kg/yr
Q_f	=	fuel use, kg/hr
MW_p	=	molecular weight of pollutant emitted, kg/kg-mole
EW_f	=	elemental weight of substance in fuel, kg/kg-mole
$OpHrs$	=	operating hours, hr/yr
Concentration of pollutant i in fuel expressed as weight percent, %		

For instance, SO₂ emissions from oil combustion can be calculated based on the concentration of sulfur in the oil. This approach assumes complete conversion of sulfur to SO₂. Therefore, for every kilogram of sulfur (EW = 32) burned, two kilograms of SO₂ (MW = 64) are emitted. The application of this EET is shown in Example 4.

Example 4 - Using Fuel Analysis Data

This example illustrates how SO₂ emissions can be calculated from oil combustion based on fuel analysis results and the fuel flow information from a lime plant. The lime plant is assumed to operate 1500 hours per year.

E_{kpy,SO_2} = may be calculated using Equation 8.

Fuel flow = 2 000 kg/hr

Weight percent sulfur in fuel = 1.17%

$$\begin{aligned} E_{kpy,SO_2} &= Q_f * \text{pollutant concentration in fuel} / 100 * (MW_p * EW_f) * OpHrs \\ &= (2\,000) * (1.17 / 100) * (64 / 32) \\ &= 46.8 \text{ kg/hr} * 1\,500 \text{ hr/yr} \\ &= 702\,000 \text{ kg/yr} \end{aligned}$$

4.4 Emission Factors

An emission factor is a tool that is used to estimate emissions to the environment. In this Manual, it relates the quantity of substances emitted from a source to some common activity associated with those emissions. Emission factors are obtained from US, European, and Australian sources and are usually expressed as the weight of a substance emitted divided by the unit weight, volume, distance, or duration of the activity emitting the substance (eg. kilograms of benzene emitted per tonne of lime produced). Sources for all emission factors cited can be found in Section 5.0 of this Manual. The emission factor ratings will not form part of the public NPI database.

When using emission factors, you should be aware of the associated emission factor rating (EFR) code and what that rating implies. An A or B rating indicates a greater degree of certainty than a D or E rating. The less certainty, the more likely that a given emission factor for a specific source or category is not representative of the source type. These ratings notwithstanding, the main criterion affecting the uncertainty of an emission factor remains the degree of similarity between the equipment/process selected in applying the factor, and the target equipment/process from which the factor was derived.

The EFR system is as follows:

A	- Excellent
B	- Above Average
C	- Average
D	- Below Average
E	- Poor
U	- Unrated

Emission factors are used to estimate a facility's emissions by the following equation:

Equation 9

$$E_{kpy,i} = [A * OpHrs] * EF_i$$

where:

$$\begin{aligned} E_{kpy,i} &= \text{emission rate of pollutant i, kg/yr} \\ A &= \text{activity rate, t/hr} \\ OpHrs &= \text{operating hours, hr/yr} \\ EF_i &= \text{uncontrolled emission factor of pollutant i, kg/t} \end{aligned}$$

Emission factors developed from measurements for a specific process may sometimes be used to estimate emissions at other sites. Should a company have several processes of similar operation and size, and emissions are measured from one process source, an emission factor can be developed and applied to similar sources. You are required to have the emission factor reviewed and approved by State or Territory environment agencies prior to its use for NPI estimations.

The following example illustrates the use of Equation 9 and data supplied in Table 8.

Example 5 - Using Emission Factors

Table 8 shows that $8000\text{kg} * 10^{-6}$ of benzene are emitted for each tonne of lime produced with a fabric filter control device in place. It is assumed that the lime plant operates for 1 500 hours per year.

$$EF_{\text{benzene}} = 0.008 \text{ kg/t}$$

$$\text{Lime production rate (A)} = 250 \text{ t/hr}$$

$$\begin{aligned} E_{kpy,\text{benzene}} &= [A * OpHrs] * EF_{\text{benzene}} \\ &= [250 \text{ t/hr} * 1\,500 \text{ hr/yr}] * 0.008 \text{ kg/t} \\ &= 3\,000 \text{ kilograms per year} \end{aligned}$$

Table 5 - Emission Factors for Lime Manufacturing - Coal and Gas Kilns¹

Source	SO ₂	Emission Factor Rating	NO _x	Emission Factor Rating	CO	Emission Factor Rating
Coal fired rotary kiln	2.7	D	1.6	C	0.74	D
- fabric filter	0.83	D	ND		ND	
- venturi scrubber	0.15	D	0.11	E	ND	
Gas fired rotary kiln	ND		1.7	E	1.1	E
Coal and gas fired kiln						
- venturi scrubber	ND		1.4	D	0.41	D
Coal and coke fired rotary kiln with venturi scrubber	ND		ND		ND	
Coal fired rotary preheater						
- dry PM controls	1.1	E	ND		ND	
- multiclone, water spray and fabric filter	3.2	E	ND		3.2	E
Gas fired calcimatic kiln	ND		0.076	D	ND	
Gas fired parallel flow regenerative kiln with fabric filter	0.006	D	0.12	D	0.23	D
Product cooler	ND		ND		ND	
Notes: 1. USEPA AP- 42 Section 11.17 (1996) 2. ND = No Data 3. Units are kg of substance emitted per tonne of lime or dolomite produced. 4. Factors represent uncontrolled emissions unless otherwise noted. 5. Mass balance on sulfur and carbon may yield a more representative emission factor for a specific facility. 6. Scientific notation is used; e.g. 7.38E-02 represents 7.38×10^{-2} or 0.0738 and 7.38E+02 represents $7.38 \times 10^{+2}$ or 738.						

Table 6 - Emission Factors for Lime Manufacturing - Raw Material Calcining¹

Process Activity	SO ₂	Emission Factor Rating	NO _x	Emission Factor Rating	CO	Emission Factor Rating
Vertical Shaft Kilns						
- uncontrolled	0.9S ²	U	0.1	U	2.0	U
- cyclone	0.9S ²	U	0.1	U	2.0	U
- multicyclones	0.9S ²	U	0.1	U	2.0	U
Vertical Double Inclined Kilns						
- uncontrolled	0.9S ²	U	0.1	U	2.0	U
- cyclone	0.9S ²	U	0.1	U	2.0	U
- multicyclones	0.9S ²	U	0.1	U	2.0	U
Parallel Flow / Counterflow Regenerative Kilns						
- uncontrolled	0.9S ²	U	0.1	U	2.0	U
- cyclone	0.9S ²	U	0.1	U	2.0	U
- multicyclones	0.9S ²	U	0.1	U	2.0	U
Annular Kilns						
- uncontrolled	0.9S ²	U	0.1	U	2.0	U
- cyclone	0.9S ²	U	0.1	U	2.0	U
- multicyclones	0.9S ²	U	0.1	U	2.0	U
Rotary Short Kilns / Air Suspension Preheater						
- uncontrolled	0.36S ²	U	1.5	U	1.0	U
- cyclone	0.36S ²	U	1.5	U	1.0	U
- multicyclones	0.36S ²	U	1.5	U	1.0	U
- ESP	0.36S ²	U	1.5	U	1.0	U
- fabric filter	0.36S ²	U	1.5	U	1.0	U
Notes:						
1. Source: USEPA AP-42 Section 11.17 (1996).						
2. 'S' indicates the Sulfur content of the fuel used in the respective processes.						

Table 7 - Emission Factors for Lime Kilns/Calciners - Inorganics¹

Substance Emitted	Type of Control	Emission Factor kg/tonne ⁴	Emission Factor Code Rating
Ammonia	FF	5.1E-03	E
Ammonia (as ammonium)	ESP	5.4E-02	D
Arsenic & compounds	ESP	6.5E-06	E
Arsenic & compounds	FF	6.0E-06	D
Beryllium & compounds	FF	3.3E-07	D
Cadmium & compounds	ESP	4.2E-06	D
Cadmium & compounds	FF	1.1E-06	D
Chromium (III) compounds	ESP	3.9E-06	E
Chromium (III) compounds	FF	7.0E-05	D
Copper & compounds	FF	2.6E-03	E
Fluoride compounds	ESP	4.5E-04	E
Hydrochloric acid	ESP	2.5E-02	E
Hydrochloric acid	FF	7.3E-02	D
Lead & compounds	ESP	3.6E-04	D
Lead & compounds	FF	3.8E-05	D
Manganese & compounds	ESP	4.3E-04	E
Mercury & compounds	ESP	1.1E-04	D
Mercury & compounds	FF	1.2E-05	D
Nickel Carbonyl		0.0E+00	D
Nickel Subsulfide		0.0E+00	D
Selenium & compounds	ESP	7.5E-05	E
Selenium & compounds	FF	1.0E-04	E
Sulfuric acid	ESP	1.00E-01	D
Sulfuric acid	FF	3.6E-03	D
Zinc & compounds	ESP	2.7E-04	D
Zinc & compounds	FF	1.7E-04	D

Note:

1. Reference: USEPA AP-42 Section 11.6 (1995).
2. ESP - Electrostatic Precipitator.
3. FF - Fabric Filter.
4. Units are kg of substance emitted per tonne of lime produced.
5. These default emission factors are based on USA emission factors that relate to USA conditions. As Australian data becomes available, these emission factors will be updated to better reflect Australian conditions. If you have more site-specific data available, you are required to have any alternate EET approved by your local environmental authority.
6. For more information on Emission Factor reliability refer to Section 4.4, Paragraph 2.
7. Scientific notation is used; e.g. 7.38E-02 represents 7.38×10^{-2} or 0.0738 and 7.38E+02 represents $7.38 \times 10^{+2}$ or 738.

Table 8 - Emission Factors for Lime Kilns/Calciners - Organics¹

CASR Number	Substance Emitted	Type of Control	Emission Factor (kg/tonne)	Emission Factor Code Rating
67-64-1	Acetone	ESP	1.9E-04	D
71-43-2	Benzene	ESP	1.6E-03	D
71-43-2	Benzene	FF	8.0E-03	E
95-52-4	Biphenyl (1,1-biphenyl)	ESP	3.1E-06	E
75-15-0	Carbon disulfide	ESP	5.5E-05	D
117-81-7	Di-(2-ethylhexyl) phthalate (DEHP)	ESP	4.8E-05	D
75-09-2	Dichloromethane	ESP	2.5E-04	E
101-41-4	Ethylbenzene	ESP	9.5E-06	D
50-00-0	Formaldehyde	FF	2.3E-04	E
78-93-3	Methyl ethyl ketone	ESP	1.5E-05	E
108-95-2	Phenol	ESP	5.5E-05	D
	Polychlorinated dioxins and furans	FF	1.5E-09	E
	Polycyclic aromatic hydrocarbons (PAHs)	FF	1.1E-03	E
100-42-5	Styrene	ESP	7.5E-07	E
108-88-3	Toluene	ESP	1.0E-04	D
1330-20-7	Xylenes	ESP	6.5E-05	D

Note:

1. Reference: USEPA AP-42 Section 11.6 (1995).
2. ESP - Electrostatic Precipitator.
3. FF - Fabric Filter.
4. Units are kg of substance emitted per tonne of lime produced.
5. These default emission factors are based on USA emission factors that relate to USA conditions. As Australian data becomes available, these emission factors will be updated to better reflect Australian conditions. If you have more site-specific data available, you are required to have any alternate EET approved by your local environmental authority.
6. For more information on Emission Factor reliability refer to Section 4.4, Paragraph 2.
7. Scientific notation is used; e.g. 7.38E-02 represents 7.38×10^{-2} or 0.0738 and 7.38E+02 represents $7.38 \times 10^{+2}$ or 738.

4.4.1 Industry-Wide Emission Factors for PM₁₀ for Lime and Dolomite Manufacturing

Emissions of PM₁₀ from the various activities in lime and dolomite production may be calculated using the following information (derived from the cement industry).

4.4.1.1 Materials Handling

- a) **unenclosed:** Equation 10 can be used to calculate the emission factor of PM₁₀ when materials handling operations are carried out in an unenclosed area. Wind speed and

moisture content of material must be taken into consideration.

Equation 10

Default formula
$$EF_{PM_{10}} = 0.75 * 0.001184 * \left[\frac{(U/2.2)^{1.3}}{(M/2)^{1.4}} \right] * ER_{PM_{10}}$$

where:

$EF_{PM_{10}}$ = emission factor, kg of PM_{10} /tonne of material handled

U = mean wind speed, m/sec

M = mean moisture content of material, %

$ER_{PM_{10}}$ = emission reduction rate. %, Table 9

NB For materials where M = 0 use default of 0.0036 kg/t of material handled.

Table 9 - Emission Reduction Factors for Materials Handling & Storage

Reduction Method	Reduction Factors ($ER_{PM_{10}}$) ²	Control Efficiency ($CE_{PM_{10}}$)
- wind breaks	0.7	30%
- water sprays	0.5	50%
- chemical suppression	0.2	80%
- enclosure (2 or 3 walls)	0.1	90%
- covered stockpiles	0.0	100%

Notes:

1. Source: The Cement Industry Federation Limited, 1998.
2. Some users may be accustomed to using Control Efficiencies (CE) in similar calculations. An ER of 0.2 equates to a CE of 80%. $ER = (1-CE/100)$

b) **bag filters venting outside:** Equation 11 can be used to calculate annual emissions of PM_{10} when using outside-venting bag filters.

Equation 11

$$E_{kpy,PM_{10}} = EF_{PM_{10}} * A * OpHrs * 10^{-6}$$

where:

$E_{kpy,PM_{10}}$ = annual emissions of PM_{10} , kg/yr

$EF_{PM_{10}}$ = emission factor for PM_{10} , mg/m³, in this case 12mg/m³

A = activity rate (hourly flow of air exhausted through the bag filter), m³/hr

OpHrs= operating hours, hr/yr

10⁻⁶ = conversion factor mg to kg.

(Where 12mg/m³ is 80% of the total particulate matter (15mg/m³vented from the bag filter.)

c) **Enclosed:** There are no emissions of PM_{10} from material handling operations when these activities are performed inside the building.

4.4.1.2 Materials Storage

Particulate matter emissions from active stockpiles due to wind can be calculated using the following equation.

Equation 12

$$E_{PM10} = EF_{PM10} * \text{area} * ER_{PM10}$$

where:

$$\begin{aligned} E_{PM10} &= \text{hourly emissions of PM}_{10}, \text{ kg/hr} \\ EF_{PM10} &= \text{emission factor of PM}_{10}, \text{ kg/ha/hr} \\ \text{area} &= \text{area of base of stockpile, ha} \\ ER_{PM10} &= \text{emission reduction of PM}_{10}, \%, (\text{Table 9}) \end{aligned}$$

NB: In the absence of available PM₁₀ data use the default EF_{PM10} = 0.3 kg/ha/hr.

Example 6 - Stockpile Emissions

A stockpile with a half-hectare base is active for the full year. Emissions of PM₁₀ are calculated using Equation 12. No information is available on site-specific factors hence the default emission factor is used. Water sprays are used to suppress dust, see Table 9.

Hourly emissions:

$$\begin{aligned} E_i &= EF_{PM10} * \text{Area} * ER_i \\ &= 0.3 * 0.5 * 0.5 \\ &= 0.075 \text{ kg/hr} \end{aligned}$$

Annual emissions:

$$\begin{aligned} E_{kpy,PM10} &= E_i * \text{OpHrs} \\ &= 0.075 * 8760 \\ &= 657 \text{ kg/year} \end{aligned}$$

4.4.1.3 Equipment Traffic

For vehicles with a gross mass greater than 5 tonnes operating on unsealed roads use the following equation for PM₁₀ emissions (kg/VKT on unsealed roads).

NB: VKT = Vehicle Kilometre Travelled.

Equation 13

$$EF_{PM10} = 0.0019 * (NW)^{3.4} * (\text{Silt})^{0.2} * ER_{PM10}$$

where:

EF _{PM10}	=	emission factor (kg / vehicle kilometre travelled)
NW	=	number of wheels
Silt	=	road surface material silt content (g/m ² as per AS3638)
ER _{PM10}	=	emission reduction (Table 10)

In the absence of available data use the default EF_{PM10} = 1.5 kg/VKT, which is 75% of total suspended particulate (TSP) matter emitted. Equation 14 can be used to calculate VKT.

Equation 14

$$\text{VKT} = D * \text{NU}$$

where:

VKT	=	vehicle kilometre travelled per year, km/yr
D	=	average distance travelled, km/vehicle/yr
NU	=	number of vehicles on-site, vehicles

Example 7 illustrates the use of Equation 14 when calculating vehicle kilometre travelled.

Example 7 - Calculating VKT

A reporting facility has 2 trucks that each travel approximately 13 000 kilometres on-site per year.

Using Equation 14:

$$\begin{aligned} \text{VKT} &= D * \text{NU} \\ &= 13\,000 \text{ km/vehicle/yr} * 2 \text{ vehicles} \\ &= 26\,000 \text{ km/yr} \end{aligned}$$

Table 10 - Emission Reduction Factors for Dust Suppression on Roads

Reduction Method	Reduction Factors (ER)	Control Efficiency (CE)
Watering (to eliminate visible dust)	0.25	75%
Chemical spraying (rate)	0.2	80%
<u>Notes:</u> 1. Source: The Cement Industry Federation Limited, 1998 2. Some users may be accustomed to using Control Efficiencies (CE) in similar calculations. An ER of 0.2 equates to a CE of 80%. ER = (1-CE/100)		

4.4.1.4 Fuel Preparation & Drying

To calculate emissions of PM₁₀ from coal drying with a dust collector use Equation 11 above (bag filters)

4.4.1.5 Lime/Dolomite Manufacturing including: Limestone/Raw Material Crushing, and Kiln Operations

To calculate the emissions from the various activities use the emission factors from

Table 11. Example 8 demonstrates how to use these emission factors.

Table 11 - Emission Factors for PM₁₀ for Lime/Dolomite Manufacturing

Component/Activities	PM ₁₀ Emission Factors (kg/tonne)
Limestone/Raw Material Crushing - material through crusher (kg/tonne) - uncontrolled - fabric filter - wet or chemical suppression - wet scrubber	 0.017 0.0002 0.0005 0.004
Kiln <i>wet process</i> - electrostatic precipitator <i>preheater kiln</i> - fabric filter - electrostatic precipitator <i>precalciner process kiln</i> - fabric filter - electrostatic precipitator	 0.3 0.1 0.1 0.1 0.1
<u>Notes:</u> 1. Source: The Cement Industry Federation Limited, 1998	

Example 8 - Lime Manufacturing PM₁₀ Generation

A lime plant uses an uncontrolled limestone crusher and a preheater kiln with an electrostatic precipitator. The throughput is 50 000 tonne of limestone per annum.

The Total emission factor from these operations (from Table 11) is:

$$\begin{aligned} \text{EF}_{\text{PM}_{10}} &= 0.017 + 0.1 \\ &= 0.117 \text{ kg/tonne of limestone} \end{aligned}$$

Annual Emissions

$$\begin{aligned} E_{\text{kpy,PM}_{10}} &= \text{EF}_{\text{PM}_{10}} * \text{Activity Rate} \\ &= 0.117 * 50\,000 \\ &= 5850 \text{ kg/yr.} \end{aligned}$$

4.5 Predictive Emission Monitoring (PEM)

Predictive emission monitoring is based on developing a correlation between pollutant emission rates and process parameters. A PEM allows facilities to develop site-specific emission factors, or emission factors more relevant to their particular process.

Based on test data, a mathematical correlation can be developed, which predicts emissions using various parameters.

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The following Emission Estimation Technique Manuals are available at the NPI Homepage (<http://www.npi.gov.au>) and from your local environmental protection agency (see the front of the NPI Guide for details):

- Emission Estimation Technique Manual for Combustion Engines; and
- Emission Estimation Technique Manual for Cement Manufacturing.